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Photoluminescent nanosensors capped with quantum dots for high-throughput determination of trace contaminants: Strategies for enhancing analytical performance

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ABSTRACT

High-throughput determination of trace contaminants has attracted a great deal of attention due to their high toxicity, hyperstability and ultra-low level. Among various analytical methods developed during the past few decades, nanosensoring techniques have become increasingly popular due to their potential for portable, rapid and real-time detection. Quantum dots (QDs) are colloidal semiconductor nanocrystals with excellent photoluminescent properties, high quantum yields and high resistance to photobleaching. Recently, QD-based photoluminescent nanosensing (plnanosensing) techniques have provided new advances in the field of contaminant determination for environmental monitoring and food quality control. This review focuses on the improvements in the analytical performances of QD-based plnanosensing techniques in order to achieve on-site rapid screening of multiple contaminants. Critical factors along with some difficulties in high-throughput determination of trace contaminants are summarized. Furthermore, the main strategies for enhancing the analytical performance of QD-based plnanosensors based on the characteristics and difficulties of trace analysis are highlighted. Finally, we discuss the difficulties in association with the use of QD-based optosensors in trace analysis and the prospective applications of this novel analytical technique in the future.

Contents

1. Introduction

Over the past few decades, a large crop of exogenous harmful materials (mycotoxins, pesticides, heavy metals, etc.) regarding their contamination in complex matrices such as foods, feeds and medicinal plants have received considerable attention due to their high occurrence in these matrices and potential toxicological risks to human and animal health and the environment, as well as the enormous challenges involved in quantifying low concentrations at ppm (mg/kg), ppb (μg/kg) or ppt (ng/kg) levels. Current analytical methods for these materials are largely restricted to laboratory instrumental analysis [1, 2] and enzyme-linked immunosorbent assay (ELISA) [3, 4]. The former requires rigorous sample preparation steps prior to analysis, including extraction, clean-up, enrichment and possible derivatisation [5] in order to improve the sensitivity and

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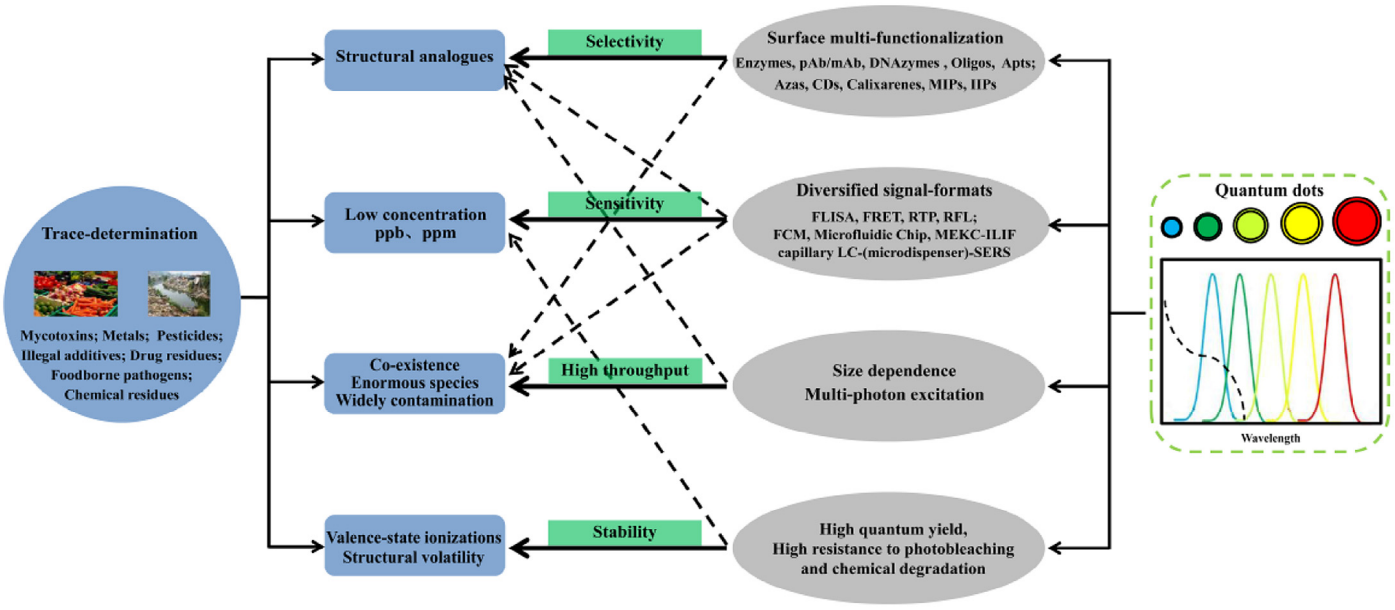

Fig. 1. Requirements and solutions of QD-based sensors for high-throughput determination of trace contaminants.

selectivity by eliminating interferences with the matrix. However, these essential steps may also decrease the analytical accuracy of various techniques due to the potential loss of trace contaminants and the increase in both cost and time associated with professional operation. In the case of ELISA, specific reactions between enzyme and antibody may face challenges of poor tolerance due to the complexity of the matrices and therefore easily produce cross-reactions and false-positive results. Therefore, convenient, ultra-sensitive and -fast analytical platforms that do not require complex preparation steps may play a significant role in multiplex high-throughput screening and on-site monitoring of trace contaminants.

Despite the fact that traditional optical analytical techniques have been widely applied for decades as potential analytical tools for the detection of trace contaminants, the matrix effects (enhancement/suppression) in complex samples for ultratrace contaminants have not been well studied. Recently, photoluminescence (PL) properties of colloidal semiconductor nanocrystals or quantum dots (QDs) in sensors have led to the development of photoluminescent nanosensors (plnanosensors) for trace determination of multiple targets [6–8]. QDs are monodisperse crystalline clusters with physical dimensions that are smaller than the bulk-exciton Bohr radius in the range of 1–20 nm and contain anywhere from 100 to 100,000 atoms per nanoparticle [9]. Multidisciplinary applications of QDs have been studied due to their unique electro-optical properties, including narrow and symmetric size-tunable PL spectra (25–40 nm), broad absorption spectra, high quantum yields, large and effective stokes shifts and high resistances to photobleaching and chemical degradation. In addition, multi-functionalization of QDs has been achieved for bioconjugating bio/chem-ligands [10, 11]. However, multiplex high-throughput determination using QDs remains challenging due to the coexcitation of multiple QD emission wavelengths by a single excitation wavelength, since the tunability of their PL emission bands depends on both the nanoparticle size (1–12 nm) and composition, which is determined by atoms in groups II–VI, III–V or IV–VI (e.g., CdSe, CdTe, InP, PbS and CdSe/ZnS) [12]. Additionally, QDs can be applied in many other techniques, such as biosensors, intelligent gene chips and nanotechnology, etc, as well as a large crop of fields, such as chemistry, microbiology, and biochemistry, to enhance specificity, sensitivity and detection speed [13–17].

Herein, we describe in detail the current status and advances in the field of QD-based portable plnanosensors for the convenient and rapid high-throughput determination of trace contaminants, allowing for enhanced analytical performance and the possibility of on-site rapid screening. In this review, the critical factors and difficulties, together with the requirements and solutions in association with determination levels of trace contaminants in foods and the environment are summarized. The main strategies for enhancing the analytical performance of QD-based plnanosensors in order to overcome these difficulties in trace determination are subsequently highlighted. Finally, future trends in the field of QD-based plnanosensors for monitoring trace contaminants are discussed (Fig. 1).

2. Characteristics of trace determination

Despite the fact that trace contaminants, such as mycotoxins, pesticides, heavy metals, and polycyclic aromatic hydrocarbons, are present in samples at ppm, ppb or ppt level, they are still associated with the disruption of ecological systems, environment hazards and threats to human health. The maximum levels of these contaminants together with the performance criteria for analytical methods have been suggested by some related organizations, such as the European Union (EU) [18].

According to the guidelines introduced by these organizations and previous reports for high-throughput analysi of trace contaminants, sampling procedures must first be optimized in order to accurately and precisely predict contaminant levels depending on lot weight, since different parts within the same sample may possess various contamination levels. In general, homogeneous and representative samples are obtained by evaluating the sampling and analytical variability using a balanced nested design [19, 20].

Moreover, a more sensitive method with a lower limit of detection (LOD) and quantitation (LOQ) will balance the problems induced by the trace and ultra-trace levels through the introduction of an extra enrichment step [21] as well as the addition of a potential derivatization process in order to improve the performance of the analytical technique [22, 5].

Additionally, trace contaminants can be widely found in various matrices which possess enormous complexity and diversity in kinds